

PMR POLYIMIDES FROM SOLUTIONS CONTAINING MIXED ENDCAPS

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Previous studies have shown that partial substitution of p-aminostyrene (PAS) for the monomethylester of endo-5-norbornene-2, 3-dicarboxylic acid (NE) lowered the cure temperature of PMR polyimides from 316 to 260° C, but the modified PMR polyimides required higher compression-molding pressures than state-of-the-art PMR-15. In this study PMR polyimides were prepared employing three endcaps: NE, PAS, and endo-N-phenyl-5-norbornene-2,3-dicarboximide (PN). The effect of PN addition on the processing characteristics and glass transition temperatures of graphite fiber-reinforced PMR composites was studied. The room temperature and short-time 316° C mechanical properties of the composites were determined. The weight loss and mechanical property retention characteristics of the composites after exposure in air at 316° C were also determined.

INTRODUCTION

Studies at NASA Lewis Research Center led to the development of a class of readily processable polyimides known as PMR polyimides (refs. 1 and 2). The commercially available version known as PMR-15 uses an alcohol solution of three monomer reactants: 4,4'-methylenedianiline (MDA), the dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE), and the monomethylester of 5-norbornene-2,3-dicarboxylic acid (NE) as an endcapping reagent. Because of its excellent processability and thermo-oxidative stability, PMR-15 has made it possible to design and fabricate composite structures for use at temperatures up to 316° C. Final curing of PMR-15 requires temperatures in the range of 288 to 316° C, preferably the higher temperature. These requirements exceed the capability of many existing autoclave facilities which were originally acquired for curing epoxy resins. A lower-curing-temperature PMR polyimide would be more compatible with existing facilities and increase the applications of PMR polyimides.

A previous study showed that the use of an alternate endcap, m-aminostyrene, lowered the final cure temperature of PMR polyimides from 316 to 260° C (ref. 3). However, the glass transition temperatures (T_g) of these polyimides were in the range of 270 to 280° C, limiting their use to temperatures not exceeding 260° C.

More recently, PMR polyimides were prepared from monomer solutions containing equimolar amounts of NE and p-aminostyrene (PAS) endcapping reagents (ref. 4). It was shown that these polyimides (designated PMR-NV polyimides) could be cured at 260° C, and exhibited T_g values in excess of 325° C. Compression-molded graphite-fiber/PMR-NV composites exhibited short-term mechanical properties as well as mechanical property retention characteristics at 316° C equivalent to those of PMR-15 composites. The PMR-NV composites, however, exhibited considerably reduced resin flow during compression molding. In order to achieve void-free composites, it was necessary to double the molding pressure compared to state-of-the-art PMR-15 composites.

The purpose of this study was to investigate the effects of incorporating an additional endcap, endo-N-phenyl-5-norbornene-2, 3-dicarboximide (PN), on the processing characteristics and properties of PMR-NV polyimides. Compression-molded

Celion 6000 graphite fiber-reinforced composites were fabricated from monomer solutions containing MDA, BTDE, equimolar amounts of NE and PAS, and various amounts of PN. The resin flow characteristics of the PMR-NV polyimides were determined. The effect of various postcure conditions on the T_g values of the composites was studied. The room temperature and short-time 316° C mechanical properties of the composites were determined. Composite weight loss and mechanical property retention characteristics as a function of exposure time in air at 316° C were also determined.

EXPERIMENTAL PROCEDURES

Monomers and PMR Solutions

The monomers used in this study are shown in table I. The dimethylester of 3,3',4,4'-benzophenonetetracarboxylic acid (BTDE) was prepared by refluxing a suspension of the corresponding dianhydride in a calculated amount of anhydrous methanol until the solid dissolved, and then for an additional 2 hr to give a 50 wt % solution of BTDE. The endo-N-phenyl-5-norbornene-2,3-dicarboximide (PN) was prepared as follows: a solution of endo-5-norbornene-2,3-dicarboxylic anhydride (41.0 g, 0.25 mole) and aniline (24.2 g, 0.26 mole) in N, N-dimethylacetamide (50 ml) was stirred at room temperature for 10 min, then heated to reflux for 1 hr. The solution was cooled to below 100° C, and water was added to cloudiness. After cooling in ice, the precipitate was filtered, washed with a mixture of water and N, N-dimethylacetamide (2:1), and dried in a vacuum at 60° C. The crude product was recrystallized from methanol to yield 52.9 g (88 %) of PN, m.p. 142.5 to 143° C. The other monomers shown in table I were obtained from commercial sources and used as received.

Prepreg solutions were prepared at room temperature by dissolving the monomers in a calculated amount of anhydrous methanol to give solutions containing 40 wt % solids. The stoichiometric ratios of the reactants used in this study are shown in table II. Differential scanning calorimetry (DSC) measurements were performed by evaporating small aliquots of the prepreg solutions to dryness, then staging for 1 hr at 150° C. The runs were performed in a commercial pressure DSC cell under 50 psi of nitrogen at a heating rate of 10° C/min.

Composite Fabrication

Prepreg tapes were made by drum winding and impregnating Celion 6000 graphite fiber with PMR solutions calculated to give composites having approximately 58 vol % fiber. The prepreg tapes were dried on the rotating drum for 1 hr, then dried further at room temperature overnight. The tapes were removed from the drum, cut into 10.16 by 10.16 cm plies and stacked unidirectionally into a preforming mold, 11 plies thick. The stack was imidized for 1 hr at 150° C under a pressure of approximately 690 Pa. After staging the stack was placed into a matched metal die and a thermocouple attached to the die. The die was inserted into a press preheated to 260° C, and a pressure of 3.45 MPa was applied when the die temperature had reached 232° C. After reaching 260° C, pressure and temperature were maintained for 2 hr. The composites were then cooled to 204° C prior to removal from the mold. The control composites (prepared from solutions without added PN) were fabricated using the same procedure, except that a molding pressure of 6.89 MPa was employed.

Composite Testing

Postcure and isothermal exposure of the composites was performed in forced air convection ovens having an air change rate of 100 cm³/min. All composites were postcured by heating to 316° C during 2 hr, holding at 316° C for 24 hr, followed by heating at 343° C for 16 hr. Prior to specimen preparation the composites were inspected for acceptance by an ultrasonic C-scan technique. The fiber content was determined by H₂SO₄/H₂O₂ digestion. Glass transition temperatures (T_g) were determined with a thermal mechanical analysis (TMA) apparatus using a penetration probe at a heating rate of 10° C/min. The probe was loaded with a 5-g weight.

Resin flow during cure was calculated according to the following equation:

$$F = \frac{W_2}{W_1 + W_2} \times 100 \quad (1)$$

where

F resin flow, wt %

W₁ weight of resin in molded composite as determined by acid digestion method

W₂ weight of staged prepreg - weight of molded composite after removal of resin flash

Isothermal exposure at 316° C was carried out using 0.508 by 10.16 cm specimens. The thickness of the specimens varied from 0.188 to 0.201 cm.

Flexural strength tests were performed in accordance with ASTM D-790 using a three-point loading fixture and a span of 5.08 cm. The span/depth ratio ranged from 25.3 to 27.0. The rate of center loading was 1.27 cm/min. Interlaminar shear strength tests were performed essentially in accordance with ASTM D-2344 at a constant span/depth ratio of 5. Elevated temperature tests were conducted in an environmental heating chamber following a 15-min soak at the test temperature. The reported mechanical property values are averages of four or more tests at each condition.

RESULTS AND DISCUSSION

It has been demonstrated (ref. 5) that addition of PN to PMR-15 increases the resin flow during compression molding. It was felt that incorporation of this additive in the PMR-NV polyimide system would increase the resin flow to a level that would permit compression molding of the composites at pressures not exceeding 3.45 MPa. It remained to be demonstrated that addition of PN in amounts up to 10 mole percent would not significantly increase the final cure temperature of the PMR-NV composites above 260° C. The monomer stoichiometry of the PMR-NV formulations used in this study is shown in table II. Differential scanning calorimetry (DSC) analysis of the various formulations indicated that it is feasible to cure the resins at 260° C. A typical DSC scan is shown in figure 1 for the PMR-NV15-PN10 formulation that had been staged for 1 hr at 150° C. The DSC scan exhibits a melt endotherm peaking at about 225° C, and a single reaction exotherm centered at about 285° C. This exotherm temperature is comparable to that of PMR-NV15 without added

PN, and is substantially lower than the cure exotherm temperature of 340° C for PMR-15 (ref. 6).

The chemistry of the PMR-NV resins prepared from solutions containing the three endcaps is shown in figure 2. Most of the methanol solvent is first evaporated at room temperature. The prepreg is then staged for 1 hr at 150° C. During this step the PAS, NE, MDA, and BTDE monomers react to form the endcapped imide oligomer structure shown in figure 2. Water and methanol are evolved during this cyclodehydration step. The PN monomer is unreactive during this step. It should be pointed out that the structure shown for the endcapped imide oligomer is an idealized one, reflecting the overall stoichiometry of each monomer formulation. It is to be expected that the actual composition consists of a mixture of oligomers having varying chain lengths.

The final cure is carried out under a pressure of 3.45 MPa at 260° C without the evolution of volatile reaction by-products to yield a crosslinked polyimide. The cure probably occurs through a very complex set of reactions. A detailed study of the cure mechanism was beyond the scope of this investigation. A few comments, however, can be made regarding the most likely cure reactions. Some possible crosslinking reactions are outlined in figure 3. If only styryl endcaps were present, a straightforward addition reaction of the vinyl groups could be expected to yield the substituted polystyrene structure shown in Scheme A. The thermal polymerization of norbornenyl endcaps follows a more complex mechanism. It is well established that the first step is a retrograde Diels-Alder reaction to yield a substituted maleimide and cyclopentadiene. It has been proposed that these species coreact to yield the structure shown in Scheme B (ref. 7).

When both styryl and norbornenyl endcaps are present, the crosslinking mechanism is very likely more complicated. It is expected that some homopolymerization of the styryl endcaps occurs. It is more likely that the styryl endcaps coreact with the Diels-Alder reversion products, as shown in Scheme C. Another possibility is the coreaction of styryl and intact norbornenyl endcaps (Scheme D).

A study of resin flow was performed on unidirectional composites prepared from unsized Celion 6000 graphite fiber and the various monomer solutions listed in table II. The prepreg was imidized at 150° C because it had been shown in the previous study (ref. 4) that imidization at temperatures above 150° C caused a significant level of resin advancement due to the presence of styryl endcaps. The imidized prepreg was placed in a mold at room temperature and inserted into a press preheated to 260° C. Pressure was applied when the temperature of the prepreg stack reached 232° C, and final cure was conducted for 2 hr at 260° C. A cure pressure of 3.45 MPa was employed in this series of experiments, compared to 8.27 MPa used for PMR-NV formulations containing no added PN (ref. 4). The results are summarized in figure 4. It can be seen that both the PMR-NV15 and PMR-NV12.5 formulations exhibited a resin flow level of less than 0.5 percent, compared to 3.85 percent for PMR-15. The incorporation of five mole percent of PN caused a significant increase of flow, to 2.6 percent for PMR-NV15-PN5 and 3.4 percent for PMR-NV12.5-PN5. Addition of ten mole percent of PN further increased the flow to levels comparable to that for PMR-15. Ultrasonic C-scan examination indicated that all panels prepared from formulations containing PN exhibited no voids.

It is well known that PMR-15 polyimides must be subjected to a free-standing postcure in air at 316° C for at least 16 hr to achieve a sufficiently high glass transition temperature (T_g) for 316° C applications. In the previous study (ref. 4) it was found that a postcure cycle of 24 hr in air at 316° C was necessary

to achieve T_g values above 320°C for PMR-NV. However, when the latter postcure cycle was used for PMR-NV composites containing PN, the T_g values did not exceed 316°C (table III). Interlaminar shear strength tests performed at 316°C exhibited thermoplastic failure. The low T_g values are not surprising, since incorporation of monofunctional PN segments is expected to decrease the crosslink density of the polymer structure and hence decrease the T_g . Consequently, a study of postcure conditions to increase the T_g of the PN-containing PMR-NV composites was performed. The results are shown in table III. It can be seen that extending the postcure time at 316°C from 24 to 48 hr did not produce a significant increase in T_g values. An attempt was made to postcure the composites at 343°C . However, blistering of the specimens occurred in several instances, even when the temperature was gradually increased to 343°C during 4 hr. It is possible that after the cure at 260°C some residual unreacted norbornenyl endcaps remain, and release volatiles during the postcure causing blister formation. When the composites were postcured for 24 hr at 316°C , followed by 343°C for 16 hr, no blistering occurred. It can be seen in table III that the T_g values of all composites were increased to levels suitable for 316°C applications.

Using the cure and postcure schedules established in the previously described resin flow and postcure studies, a new series of 10.16 by 10.16 cm unidirectional composites were fabricated from unsized Celion 6000 graphite fibers and each of the resins listed in table II. Ultrasonic C-scan examination of the composites after postcure indicated that they were free of defects. The room temperature and initial 316°C mechanical properties of the composites are summarized in table IV. It can be seen that both the 25°C properties and short-term 316°C properties of the PMR-NV composites containing PN are essentially equivalent to those of the control, PMR-NV15, composite. Furthermore, the PMR-NV composite properties are equivalent to those of state-of-the-art PMR-15 composites (ref. 4).

The weight loss characteristics of the composites after exposure in air at 316°C are shown in figure 5. There appears to be a slight trend toward higher weight loss with increasing PN content, as well as decreasing formulated molecular weight values. This can be attributed to increase of alicyclic content in both cases. However, the differences are not considered to be significant.

The interlaminar shear strength (ILSS) retention characteristics of the composites after exposure and testing in air at 316°C are compared in figure 6. The composites prepared from formulations containing PN exhibit slightly lower ILSS values after long term exposure at 316°C , compared to those of the control sample. This is probably due to the lower matrix modulus values resulting from incorporation of the monofunctional PN segments into the polymer chain. It has been shown (ref. 8) that composite ILSS is influenced by the modulus of the polymer matrix. Therefore, the lower ILSS values are probably due to the lower matrix modulus resulting from incorporation of the monofunctional PN segments into the polymer chain.

The flexural strength retention characteristics of the composites are shown in figure 7. All composites exhibit an increase in flexural strength up to approximately 900 hr of exposure at 316°C . This increase can be attributed to an increase of favorable crosslinking reactions of the resin matrix. The PN-containing composites exhibit slightly lower flexural strength values during this period, but on further exposure their flexural strength values are essentially equivalent to those of the control composite.

The flexural modulus values of the PN-containing composites (shown in figure 8) coincide quite closely with those of the control. This is to be expected, since composite modulus is a fiber-dominated property.

CONCLUSIONS

Based on the results of this investigation, several conclusions can be drawn. PMR polyimide composites prepared from monomer solutions containing equimolar amounts of the monomethylester of endo-5-norbornene-2, 3-dicarboxylic acid (NE) and p-aminostyrene (PAS) and 5 to 10 mole percent of endo-N-phenyl-5-norbornene-2, 3-dicarboximide (PN): (1) can be compression-molded at 260° C compared to 316° C for state-of-the-art PMR-15 composites; (2) exhibit resin flow comparable to that of PMR-15 composites; (3) require a postcure temperature of 343° C compared to 316° C for PMR-15 composites; (4) exhibit room temperature and short-term 316° C mechanical properties essentially equivalent to those of control composites; (5) exhibit slightly lower interlaminar shear strength values during 1500 hr of exposure and slightly lower flexural strength values during 900 hr of exposure in air at 316° C, compared to those of control composites.

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TABLE I. - MONOMERS USED FOR POLYIMIDE SYNTHESIS

STRUCTURE	NAME	ABBREVIATION
	MONOMETHYL ESTER OF ENDO-5-NORBORNENE-2,3-DICARBOXYLIC ACID	NE
	P - AMINOSTYRENE	PAS
	ENDO-N-PHENYL-5-NORBORNENE-2,3-DICARBOXIMIDE	PN
	DIMETHYL ESTER OF 3,3',4,4'-BENZO-PHENONETETRACARBOXYLIC ACID	BTDE
	4,4'-METHYLENEDIANILINE	MDA

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TABLE II. - COMPOSITION OF PMR-NV POLYIMIDES

RESIN	PN MOLE percent	MOLES OF REACTANTS				
		PAS	NE	MDA	BTDE	PN
PMR-NV 15 (CONTROL)	0	1	1	2.5	2.5	0
PMR-NV 15-PN 5	5	1	1	2.5	2.5	0.368
PMR-NV 15-PN 10	10	1	1	2.5	2.5	.778
PMR-NV 12.5-PN 5	5	1	1	2	2	.316
PMR-NV 12.5-PN 10	10	1	1	2	2	.667

CS-63-0957

TABLE III. - GLASS TRANSITION TEMPERATURES OF CELION 6000 GRAPHITE FIBER/PMR-NV POLYIMIDE COMPOSITES

RESIN	T _g , °C AFTER POSTCURE		
	24 hr @ 316° C	48 hr @ 316° C	24 hr @ 316° C + 16 hr @ 343° C
PMR-NV 15	328	332	358
PMR-NV 15-PN 5	314	320	353
PMR-NV 15-PN 10	303	308	342
PMR-NV 12.5	330	335	358
PMR-NV 12.5-PN 5	316	321	344
PMR-NV 12.5-PN 10	304	310	341

CS-83-0961

TABLE IV. - MECHANICAL PROPERTIES OF CELION 6000 GRAPHITE FIBER/PMR-NV POLYIMIDE COMPOSITES^a

RESIN	INTERLAMINAR SHEAR STRENGTH, MPa		FLEXURAL ^b STRENGTH, MPa		FLEXURAL ^b MODULUS, GPa	
	25° C	316° C	25° C	316° C	25° C	316° C
PMR - NV 15	113	50.3	1740	960	127	116
PMR-NV 15-PN 5	109	49.6	1750	950	121	112
PMR-NV 15-PN 10	112	49.6	1710	910	120	112
PMR-NV 12.5-PN 5	112	49.6	1850	940	123	115
PMR-NV 12.5-PN 10	110	48.9	1860	900	125	113

^a POSTCURED 24 hr IN AIR AT 316° C PLUS 16 hr IN AIR AT 343° C

^b NORMALIZED TO 60 v/o FIBER

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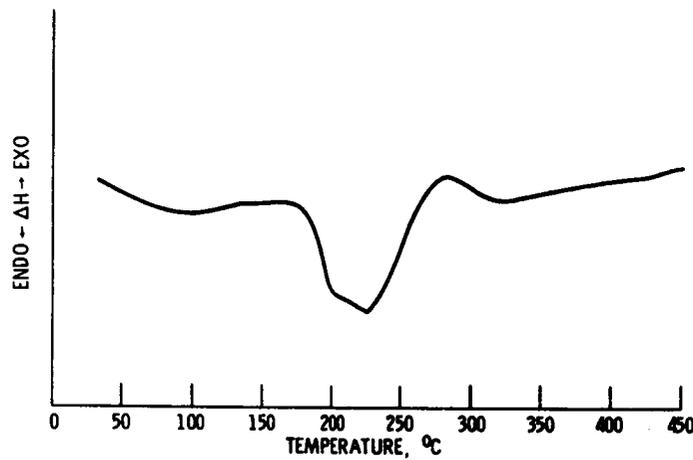


Figure 1. - DSC scan of PMR-NV15-PN10 prepreg staged for 1 hr at 150° C.

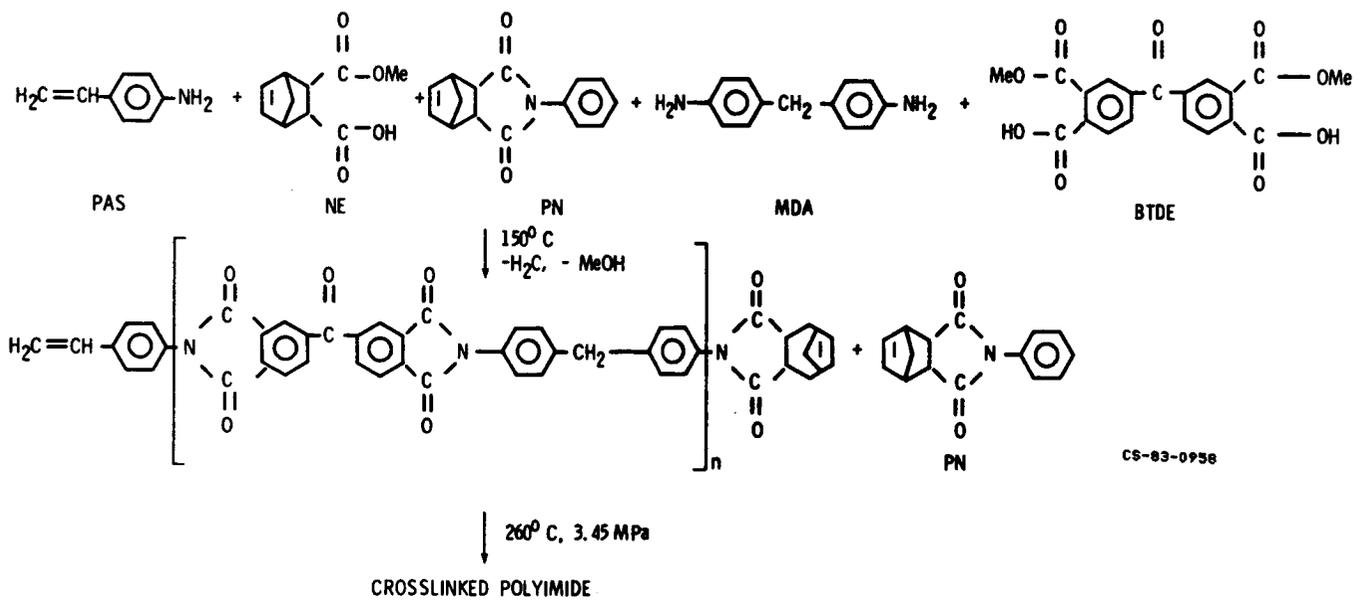


Figure 2. - PMR-NV polyimide chemistry.

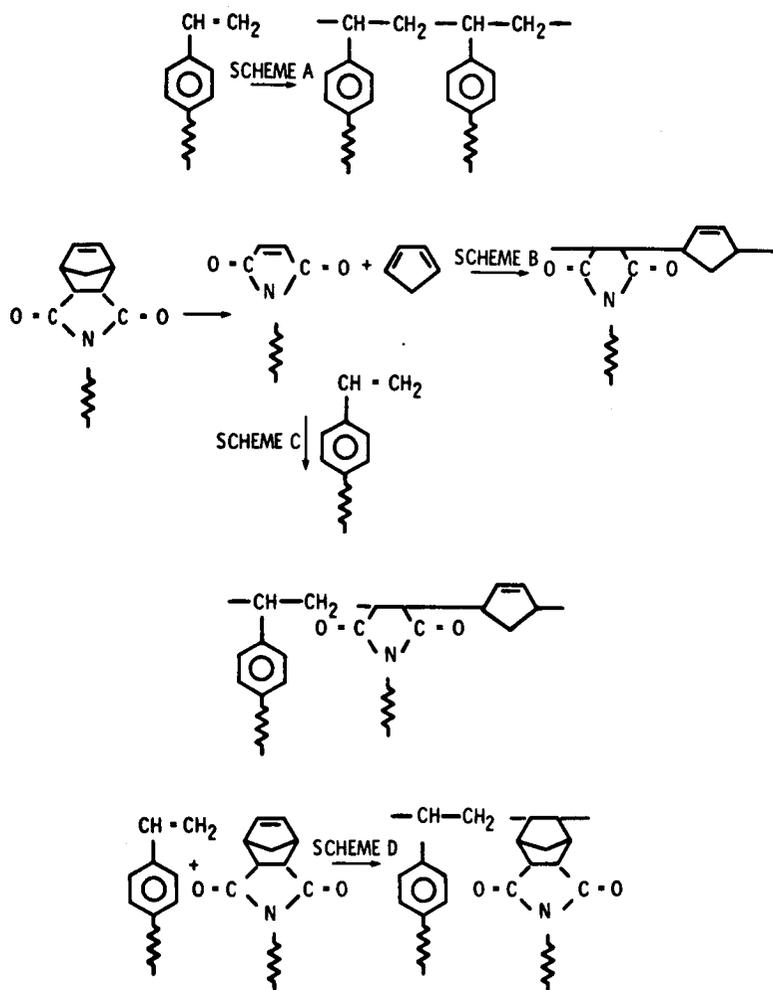


Figure 3. - Possible crosslinking reactions of PMR-NV polyimides.

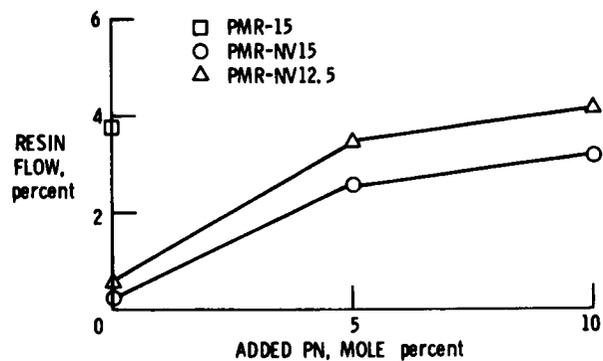
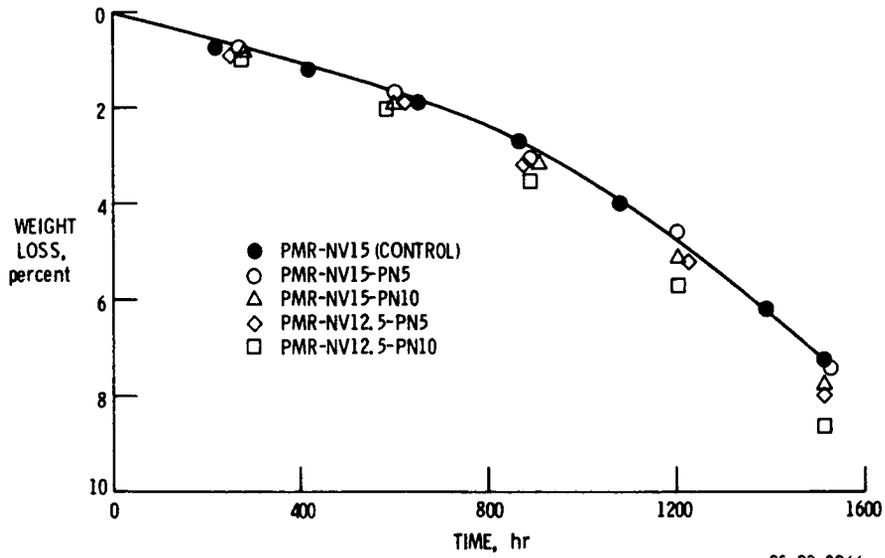
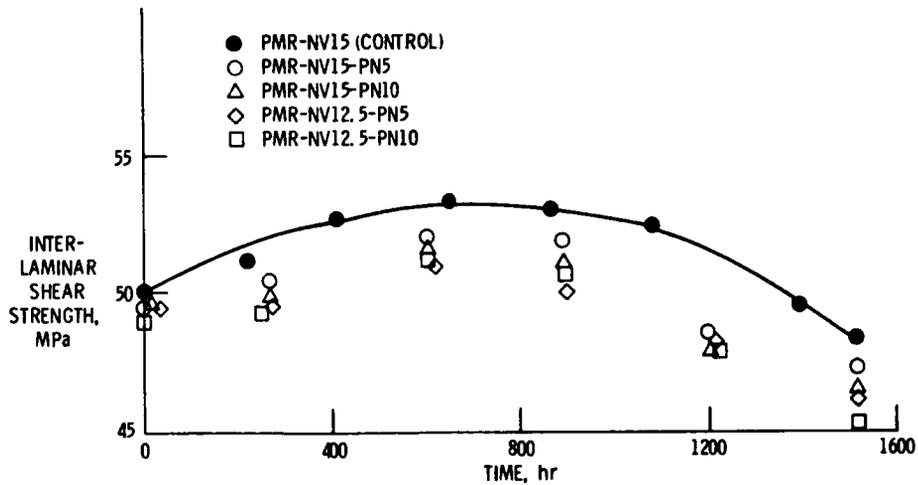


Figure 4. - Resin flow of PMR-NV polyimides.



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Figure 5. - Weight loss of Celion 6000 graphite fiber/PMR-NV polyimide composites in air at 316° C.



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Figure 6. - Interlaminar shear strength of Celion 6000 graphite fiber/PMR-NV polyimide composites exposed and tested in air at 316° C.

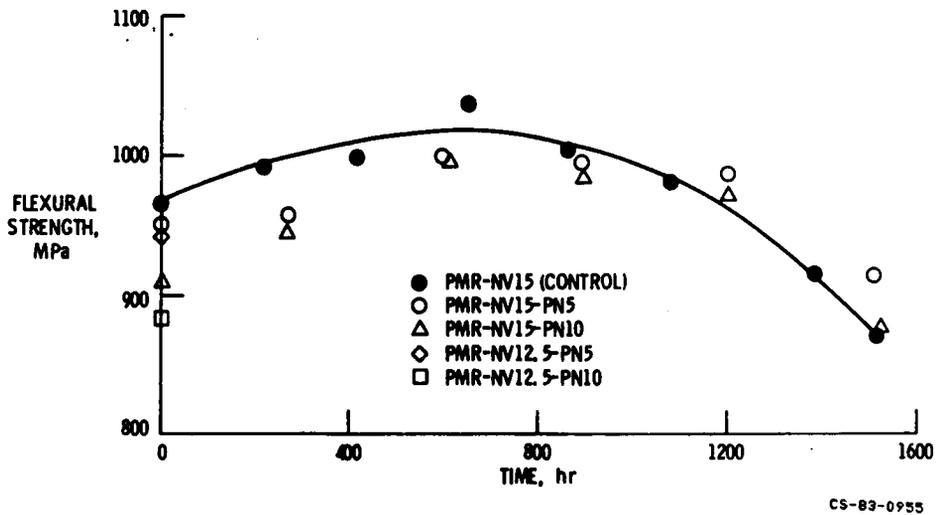


Figure 7. - Flexural strength of Celion 6000 graphite fiber/PMR-NV polyimide composites exposed and tested in air at 316° C.

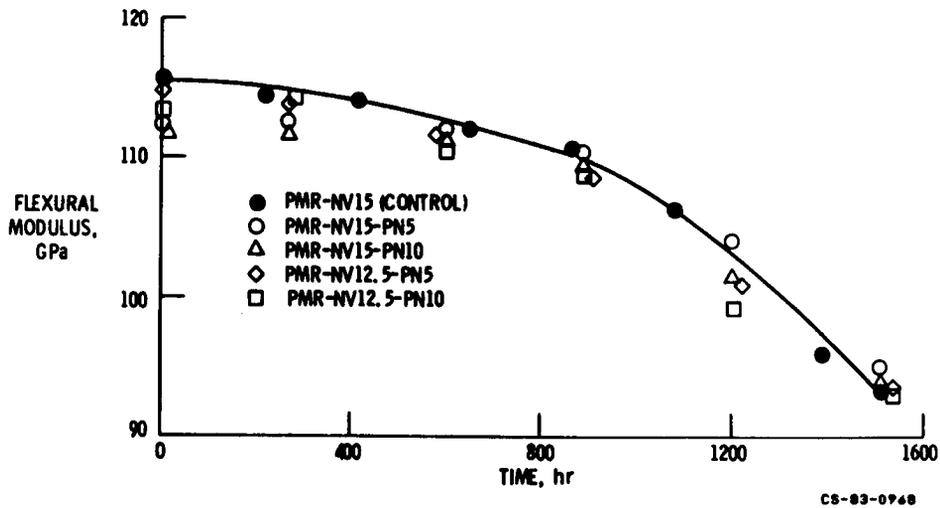


Figure 8. - Flexural modulus of Celion 6000 graphite fiber/PMR-NV polyimide composites exposed and tested in air at 316° C.